

curing and hardening the roller portion while arranged on the rotary shaft;

DS/Cond
wherein the workability improver is a material that has a property of improving moldability, mold-releasability, cutting/grinding workability, and grinding accuracy of the green press molded bodies.--

REMARKS

This application has been amended so as to place it in condition for allowance at the time of the next Official Action.

The Official Action rejects claims 1-7 under 35 USC §112, second paragraph, as being indefinite. Reconsideration and withdrawal of this rejection are respectfully requested for the following reasons:

The Official Action states that "the molded body" as recited in claim 1 lacks antecedent basis. The Official Action further objects to claim 1 in that the last two lines appear to repeat the limitation recited in lines 3-8 of such claim. Please note that applicants have amended the claim as necessary in order to eliminate the bases for this rejection and objection.

The Official Action rejects claims 1 and 2 under 35 USC §102(b) as being anticipated by FUCHS et al. 5,257,965. The Official Action further rejects claims 3-7 under 35 USC §103(a) over the same FUCHS et al. reference. Reconsideration and withdrawal of both rejections are respectfully requested for the following reasons:

The term "workability improver" is defined on page 20, lines 6-8 of the present specification. That is, the workability improver is a material that improves moldability, mold-releasability, cutting/grinding workability and grinding accuracy of the molded body obtained from the hydraulic composition.

The Official Action states that the hydraulic composition in FUCHS et al., which allegedly comprises a hydraulic powder, a non-hydraulic powder and a workability improver (the additives and activators described by the applied reference), is the same as that used in the claimed invention. Applicants respectfully suggest that such characterization is inaccurate, particularly in light of the definition of the term "workability improver".

FUCHS et al. state "It has furthermore been proposed to build up the shell of the press roller in the form of a hardened body of a hydraulic composition, ... the additives, activators etc. are added in addition to water" and refers to German Patent Disclosure Document 36 17 316 on column 1, line 59 to column 2, line 3. As to the additives, activators, etc. the identified

German	Patent	Disclosure	Document	recites
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"Wasserreduktionsmittel" (water-reducing agent) as an additive
in claim 2 and also on page 8, line 2. Please note that this German Patent Disclosure Document relates to the rollers in a water-squeezing section of a paper-producing machine different
from the paper feed roller according to the present invention for
a printer, facsimile, copier or the like.

Applicants enclose herewith an excerpt from Cement Chemistry by H. F. W. Taylor, pages 352-357 of which explain the meaning of the term "water reducers" (water-reducing agent) as it pertains to cement. This provides insight into the term as it is used by the identified German reference, and the applied FUCHS et al. reference that refers to it.

In general, "workability", when viewed in the context of cement chemistry, is used to mean the degree of difficulty with which concrete is cast, and to indicate concrete material-separation resistance, flow ability and viscosity. Workability refers to generally empirical properties, and the softer the concrete, the better the workability. Thus, workability is often expressed by slump value. As is clearly evident from the definition offered by the present application, the term "workability improver" for the material which improves moldability, mold-releasability, cutting/grinding workability and grinding accuracy of the molded body bears no resemblance to the meaning in the context of concrete chemistry.

The workability improver used in the present invention improves moldability, mold-releasability, cutting/grinding workability and grinding accuracy of the molded body obtained from the hydraulic composition, and has nothing whatsoever to do with the ordinary additive or activator ("water-reducing agent" as in the above German Patent Disclosure Document).

FUCHS et al. never even remotely suggest that the additive or activator could be replaced by the workability

improver as in the claimed invention. This is clear from the fact that the German Patent Disclosure Document cited in FUCHS et al. recites the water-reducing agent. The water-reducing agent is a chemical mix agent which reduces a unit amount of water necessary for obtaining a given slump value.

The claimed paper feed roller is a roller required to accurately feed papers in printers, facsimiles, copiers, etc. In such paper feed rollers, deviation accuracy, antivibration properties and light weight are necessary. This is a reason why the workability improver is incorporated into the hydraulic composition in the claimed invention to improve moldability, mold-releasability, cutting/grinding workability and grinding accuracy of the molded body obtained from the hydraulic composition. As to grindability and grinding accuracy, specific examples are noted the present application.

Please note that the water reducer is generally composed mainly of a surface-active agent, which ionically dissociates in water to show strong anion activity. The active anions are absorbed on surfaces of cement particles to form dual diffusion-electric layers on the cement particles. Thus, the cement particles are diffused due to the electrostatic repulsion of the dual layers. Water and air bubbles inside flock are released, which contributes improved flow ability of the cement paste and consequently the workability of the cement.

In ASTM C494-82, there are specified A-type, D-type and E-type water reducers. It is clear that these water reducers do

not correspond to those recited in claim 7 of the present application.

The press roller of FUCHS et al. (e.g. diameter of 0.3 to 1.5 meters and a length of up to 9 meters; see column 1, lines 5-8) is required to have high compression strength. From this standpoint, the skilled person in the art would never consider the workability improver used in the claimed paper feed roller for use in fine machines such as printers, facsimiles and copiers.

Furthermore, please note that applicants have amended independent claim 1 to recite not only that the cylindrical roller comprises a mixture of hydraulic composition comprising a hydraulic powder and a non-hydraulic powder and a workability improver, but also that the workability improver is a material that has a property of improving moldability, mold-releasability, cutting/grinding workability, and grinding accuracy of a molded body obtained from the hydraulic composition.

Given this recitation of the workability improver that is recited as a component of the cylindrical roller, it is respectfully suggested that the applied FUCHS et al. reference fails to either anticipate or render obvious the invention recited either in claim 1 or in the claims that depend therefrom.

The Official Action rejects claims 8 and 9 under 35 USC §103(a) over FUCHS et al. in view of KADOMATSU et al. 4,586,699. Reconsideration and withdrawal of this rejection are respectfully requested for the following reasons:

The Official action states that KADOMATSU et al. teach press molding molded bodies in a roller, with reference to Figure 7. Applicants note, however, that the teachings of this reference cannot reasonably be so construed. It is instructive to consider the passage beginning in column 5, line 18 of KADOMATSU et al.:

As shown in FIG. 7a, a rubber material or NBR in the present embodiment is mixed with ferrite powder and, if desired, with a curing agent, and then the mixture 5' is passed between a pair of mixing rollers 8 in rotation thereby forming a sheet 5" of rubber magnet material uniform in composition. Then, as shown in FIG. 7b, the sheet 5" of rubber magnet material is placed around the roll 4, and, thereafter, the roll 4 wrapped with the sheet 5" is put into a mold cavity 9a defined by a press mold 9. Under the condition, pressure and heat are applied to the press mold 9 to cure the sheet 5". As a result, there is formed a rubber layer 5' having a substantially uniform thickness $t_{sub.5}$ ' on the peripheral surface of the roll 4, as shown in FIG. 8b.

In KADOMATSU et al., the shaped (or molded) "flexible or bendable" sheet is first prepared, then wrapped around the roll, and closely press fitted there around, followed by curing. If the present rejected claims are to be read on this reference at all, the recited "molding" may correspond to "forming a sheet 5" of rubber magnet material in KADOMATSU et al. The molded body in claim 8 cannot be bent at all. Such a method cannot be applied to the molding of the hydraulic composition, which is quite obvious to the skilled person in the art.

Accordingly, one cannot reasonably combine FUCHS et al. with KADOMATSU et al. to produce a unified teaching of any method, let alone that recited by the present claims.

Furthermore, applicants have amended claim 8 to further recite that the workability improver is a material that has a property of improving moldability, mold-releasability, cutting/grinding workability, and grinding accuracy of the molded bodies. The primary FUCHS et al. reference fails to teach or suggest this characteristic, as noted in detail in the first obviousness rejection, and the secondary reference fails to overcome this shortcoming.

The Official Action rejects claims 10 and 11 under 35 USC §103(a) over YAMAMOTO et al. 5,649,362 in view of REBRES et al. 5,267,008. Reconsideration and withdrawal of this rejection are respectfully requested for the following reasons:

YAMAMOTO et al. disclose a method for producing a permanent magnet member composed of an integral sintered body, comprising the steps of:

- (a) extruding an elongated cylindrical body;
- (b) cutting said elongated cylindrical body into individual cylindrical bodies each having a predetermined axial length;
- (c) after drying, subjecting the cut cylindrical body to a sintering process to produce a sintered cylindrical body;
- (d) grinding an outer surface of said sintered cylindrical body;
- (e) machining opposite ends of said sintered cylindrical body to form the shaft portions; and

(f) providing a plurality of magnetic poles extending axially and arranged circumferentially on the outer surface of said cylindrical center portion of said sintered cylindrical body. See, for example, claim 1.

In contrast, according to the claimed invention, a paper feed roller is produced by the following steps:

(a) forming a plurality of cylindrical green bodies by press molding;

(b) releasing the green press molded bodies;

(c) inserting the rotary shaft through the holes of the green bodies;

(d) connecting adjacent said green bodies; and

(e) forming a cylindrical body through curing and hardening.

YAMAMOTO et al. therefore clearly fail to teach or suggest the recited method. Furthermore, the secondary REBRES et al. reference fails to overcome the deficiencies of the primary reference.

The Official Action states that YAMAMOTO et al. teach forming cylindrical green molded bodies by molding a mixture of a hydraulic composition comprising a hydraulic powder, and a non-hydraulic powder and a workability improver. Applicants suggest, however, that such construction of the reference is incorrect.

YAMAMOTO et al. must use a sinterable starting material, not a hydraulic composition as in the claimed invention. For such a sinterable material, YAMAMOTO et al. state

in column 4, line 64 to column 5, line 12 that the method is based upon use of "a basic composition expressed by the formula $MO_nFe_2O_3$ wherein M represents at least one element selected from the group consisting of Ba, Sr and Pb, and n is 5-6. The ferrite particles are mixed with a liquid such as alcohol, water etc. to prepare a muddy or pasty starting material suitable to be extruded."

The above muddy or pasty starting material quite differs from the hydraulic composition used in the claimed invention. This is correct even in view of additional ingredients disclosed in column 5, lines 33-35 (B_2O_3 , CaO and SiO_2). The composition of YAMAMOTO et al. is used to produce an extruded body composed of the ferrite particles and the binder.

The producing method of YAMAMOTO et al. including the sintering step is indispensable for the producing of the permanent magnet member. Sintering cannot be omitted from the YAMAMOTO et al. method.

The Official Action states that REBRES et al. teach forming a plurality of press molded bodies 81, 82 each having a hole at a central portion by press molding, inserting a rotary shaft 83 through the holes of the plurality of cylindrical bodies, and connecting adjacent bodies. However, in REBRES et al., a composite feed roll means comprises cylindrical portions of silicone and isoprene materials mounted alternatively around a rotary shaft. REBRES et al. do not seem to disclose that "press-molded bodies" are connected together around the rotary shaft.

Accordingly, applicants respectfully suggest that the combination of references fails to render obvious the claims in their current form.

Furthermore, please note that applicants have amended claim 10 to specifically recite the characteristics of the workability improver, as with claims 1 and 8. These features are clearly neither taught nor suggested by either of the applied references.

The Official Action rejects claims 12-17 under 35 USC §103(a) over FUCHS et al. in view of KADOMATSU et al. and KELLER 4,583,272. Reconsideration and withdrawal of this rejection are respectfully requested for the following reasons:

As mentioned above, according to KADOMATSU et al., the shaped (or molded) "flexible or bendable" sheet is first prepared, then wrapped around the roll, and closely press fitted therearound, followed by curing. As also discussed above, "molding" in the claimed invention may correspond to "forming a sheet 5" rubber magnet material in KADOMATSU et al. The molded body in claim 8 cannot be bent at all. Such a method of KADOMATSU et al. cannot be applied to the molding of the hydraulic composition, which would be clear to the skilled person in the art.

KELLER merely teaches two rotary shaft portions as shown in Figures 5-7.

As mentioned above, FUCHS et al. completely differ from the claimed invention, and in addition KADOMATSU et al. cannot be

combined with FUCHS et al. as mentioned above. Therefore, even combination of FUCHS et al. with KADOMATSU et al. and KELLER cannot make the claimed invention obvious.

Furthermore, applicants have amended independent claim 12 to recite specific characteristics of the workability improver, which features are neither taught nor suggested by any of the applied references.

The Official Action rejects claims 18-21 and 23 under 35 USC §103(a) over YAMAMOTO et al. in view of REBRES et al. and TAKEI et al. (EP 0 734 873 A2). Reconsideration and withdrawal of this rejection are respectfully requested for the following reasons:

Applicants note that while the introduction to this rejection identifies TAKEI et al. as a secondary reference, the narrative portion of the rejection refers instead to KELLER.

In any event, applicants have amended independent claim 18 to recite characteristics of the workability improver that are neither taught nor suggested by the applied references, including either TAKEI et al. or KELLER. Furthermore, the arguments advanced above in connection with other rejections based on such references are equally applicable to the present rejection.

The Official Action rejects claim 22 under 35 USC §103(a) over YAMAMOTO et al. in view of REBRES et al. and TAKEI et al. and further in view of FUCHS et al. Reconsideration and withdrawal of this rejection are respectfully requested for the following reasons:

As stated above, the YAMAMOTO et al. and REBRES et al. references fail to combine to render obvious the present invention. Further, the TAKEI et al. reference fails to cure the deficiencies and discrepancies existing in the combination of YAMAMOTO et al. with REBRES et al. in connection with the claimed invention. This is clearly demonstrated by the following:

TAKEI et al. relate to a method for forming a roller, comprising the steps of:

(a) mounting a shaft to a recess provided on one end wall of one half-split body; (b) engaging the other half-split body with the one half-split body; (c) injecting a core body forming fluid from an injection hole provided on other end wall of each half-split body; and (d) attaching a stopper body serving as an aligning member having a through hole in the middle thereof for inserting the shaft thereinto, such that a stopper projecting on an outer circumference thereof is fitted into said injection hole. See, for example, claim 1. Thus, TAKEI's method cannot be adapted to combine with that of YAMAMOTO et al. and REBRES et al.

Furthermore, claim 22 depends ultimately from claim 18, which claim applicants have amended as described above.

The Official Action states that applicants argue that the YAMAMOTO et al. reference teaches sintering, and further argues that sintering is not curing or hardening. The Official Action goes on to point out that in column 5, lines 3-5 and lines 55-59 of YAMAMOTO et al., the mixture starts off as muddy or pasty and is then hardened and cured because it becomes solid.

Applicants first must emphasize that sintering, which has as its accepted definition the formation of a coherent mass by heating without melting, completely differs from hydraulic curing and hardening in terms of the reacting and solidifying mechanisms.

As to YAMAMOTO et al., a muddy or pasty mixture of ferrite particles, alcohol, water, etc. is extruded, the liquid components are removed from the extruded body, and a hardened body is obtained by sintering the resultant at 1,150°C to 1,300°C. Therefore, neither the general definition of sintering nor the particular implementation of sintering taught by YAMAMOTO et al. serves to teach or suggest the "curing and hardening of molded bodies" of the present claims.

In light of the amendments described above and the arguments offered in support thereof, applicants believe that the present application is in condition for allowance and an early indication of the same is respectfully requested.

If the Examiner has any questions or requires further clarification of any of the above points, the Examiner may contact the undersigned Attorney so that this application may continue to be expeditiously advanced.

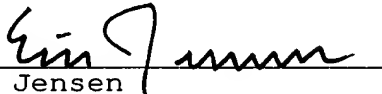
UCHIDA et al. S.N. 09/486,262

Attached hereto is a marked-up version of the changes made to the claims. The attached page is captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE."

Respectfully submitted,

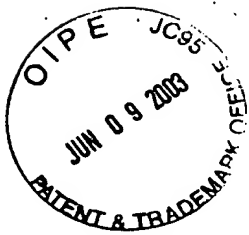
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June 9, 2003



UCHIDA et al. S.N. 09/486,262

VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE CLAIMS:

Claim 1 has been amended as follows:

--1. (thrice amended) A paper feed roller comprising:

a rotary shaft, and

a cylindrical roller [portion prepared by press molding] that comprises a mixture of hydraulic composition comprising a hydraulic powder and a non-hydraulic powder and a workability improver [and then curing and hardening the molded body], said cylindrical roller portion being integrated with an outer periphery of the rotary shaft[,

wherein the cylindrical roller comprises a mixture of a hydraulic composition];

wherein the workability improver is a material that has a property of improving moldability, mold-releasability, cutting/grinding workability, and grinding accuracy of a molded body obtained from the hydraulic composition.--

Claim 8 has been amended as follows:

--8. (thrice amended) A method for producing a paper feed roller, comprising the steps of:

forming a plurality of cylindrical molded bodies by press molding a mixture of a hydraulic composition comprising a hydraulic powder and a non-hydraulic powder and a workability improver, each of the cylindrical molded bodies having a hole at a central portion through molding the hydraulic composition, releasing, curing and hardening the molded bodies,

inserting a rotary shaft through the holes of the plurality of cylindrical molded bodies, and

connecting adjacent said cylindrical molded bodies, and thereby integrally forming a cylindrical roller portion around an outer peripheral surface of the rotary shaft;

wherein the workability improver is a material that has a property of improving moldability, mold-releasability, cutting/grinding workability, and grinding accuracy of the molded bodies.--

Claim 10 has been amended as follows:

--10. (thrice amended) A method for producing a paper feed roller, comprising the steps of:

forming a plurality of cylindrical green press molded bodies each having a hole at a central portion by press molding a mixture of a hydraulic composition comprising a hydraulic powder and a non-hydraulic powder and a workability improver,

releasing the green press molded bodies,

inserting a rotary shaft through the holes of the plurality of the cylindrical green press molded bodies,

connecting adjacent said cylindrical green press molded bodies, and

forming a cylindrical shaped body through curing and hardening the connected cylindrical green press molded bodies, so as to integrally form a cylindrical roller portion around an outer peripheral surface of the rotary shaft;

wherein the workability improver is a material that has a property of improving moldability, mold-releasability, cutting/grinding workability, and grinding accuracy of the green molded bodies.--

Claim 12 has been amended as follows:

--12. (thrice amended) A method for producing a paper feed roller, comprising the steps of:

forming a cylindrical roller portion from a cylindrical press molded body shaped through press molding a mixture of a hydraulic composition comprising a hydraulic powder and a non-hydraulic powder and a workability improver,

releasing, curing and hardening the press molded body,

arranging two rotary shaft portions to be concentric with an outer peripheral surface of the cylindrical roller portion, and

attaching the two rotary shaft portions to opposite end portions of the cylindrical roller portion, the two rotary shaft portions being aligned with each other, so as to form a rotary shaft by the two rotary shaft portions;

wherein the workability improver is a material that has a property of improving moldability, mold-releasability, cutting/grinding workability, and grinding accuracy of the press molded body.--

Claim 18 has been amended as follows:

--18. (thrice amended) A method for producing a paper feed roller, comprising the steps of:

press molding a mixture of a hydraulic composition comprising a hydraulic powder and a non-hydraulic powder and a workability improver to produce cylindrical green press molded bodies,

releasing the cylindrical green press molded bodies,
forming a cylindrical roller portion from the cylindrical green press molded bodies,

arranging two rotary shaft portions to be concentric with an outer peripheral surface of the cylindrical roller portion, and

attaching the two rotary shaft portions to opposite end portions of the cylindrical roller portion, the two rotary shaft portions being aligned with each other, so as to form a rotary shaft by the two rotary shaft portions, and

curing and hardening the roller portion while arranged on the rotary shaft;

wherein the workability improver is a material that has a property of improving moldability, mold-releasability, cutting/grinding workability, and grinding accuracy of the green press molded bodies.--

Cement Chemistry

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11.3.2 Grinding aids

Grinding aids are sometimes used in clinker grinding, to decrease the energy required to achieve a given fineness of grinding or throughput. Massazza and Testolin (M103) reviewed their use. They are surfactants of various kinds, of which amines and polyhydric alcohols are possibly the most effective, and the amounts added are normally 0.01–0.1% on the weight of clinker. They appear to act mainly by decreasing agglomeration, though it has been suggested that they also aid fracture by preventing incipient microcracks from healing. There are conflicting reports on their effects on setting times, early strength and other properties. Grinding aids are clearly taken up by the anhydrous phases, and it is probably significant that the more effective are of different chemical types from retarders and water reducers, which are taken up mainly or entirely by the hydration products.

11.4 Water reducers and superplasticizers

11.4.1 Water reducers

Water-reducing agents, also called plasticizers, allow a given degree of workability to be achieved at a lower w/c ratio. Conventional water reducers allow w/c to be decreased by 5–15%. To achieve greater decreases, they would have to be used at concentrations that would also cause excessive retardation, excessive air entrainment or flash setting. More powerful water reducers, called superplasticizers, allow w/c to be decreased by up to about 30%; these are considered in Section 11.4.2.

Water reducers act by adsorption at the solid-liquid interface, in this respect resembling retarders. There is a wide overlap between the two properties, many retarders being in varying degrees water reducers and vice versa. Both properties also overlap to some extent with that of air entrainment, which is promoted by admixtures that act at the air-liquid interface. Conventional water reducers are typically added as solutions in concentrations of up to 0.2% on the weight of cement. Calcium and sodium lignosulphonates are widely used both as retarders and as water reducers. Their retarding effect can be decreased by treatment to lower the content of sugars and sugar acids, and can be further decreased or reversed by blending with an accelerator, or enhanced by blending with a stronger retarder. Compounds that decrease air entrainment may also be added. Other materials used as water reducers include salts of hydroxy carboxylic acids, hydrolysed carbohydrates, and hydrolysed proteins.

In general, water reducers are effective with Portland, composite and

calcium aluminate cements. Many of the characteristics of retarders, described in Section 11.2.1, apply also to water reducers, and for the same reasons; thus, they are most effective if added a few minutes after mixing, and, in some cases at least, with cements low in aluminate phase and alkali. The workability of any fresh concrete decreases with time after mixing, but this effect, which is called slump loss, is more marked if a water reducer is used. The slump nevertheless remains higher than if the latter was absent. Slump loss is caused by the slow commencement of the hydration reactions, and its increased magnitude in concrete containing water reducers is probably due to the gradual absorption of the admixture by the hydration products. Delay in adding the admixture until a few minutes after mixing minimizes it.

11.4.2 Superplasticizers

Superplasticizers are also called high-range water reducers. The marked lowering of w/c ratio that they allow makes it possible to produce high-strength concretes, especially if the mix also includes microsilica. Alternatively, the use of superplasticizers at normal w/c ratios allows the production of flowing concrete that is self-levelling and can readily be placed by such methods as pumping or continuous gravity feed through a vertical pipe. The greater effect compared with conventional water reducers is due to the fact that they can be used in higher concentrations, which can be over 1% on the weight of cement, without causing excessive retardation or air entrainment. If used in similar concentrations to conventional water reducers, the degrees of water reduction obtained are also similar.

Three principal types of superplasticizer are in common use, viz. salts of sulphonated melamine formaldehyde polymers (SMF), salts of sulphonated naphthalene formaldehyde polymers (SNF), and modified lignosulphonate materials. Most of the available information relates to the first two types, which will alone be considered here. Both are linear anionic polymers with sulphonate groups at regular intervals (Fig. 11.3). The SMF materials are high molecular weight polymers, their most effective components possibly having molecular weights of about 30 000. The SNF materials are less highly polymerized, and have chains some 10 units in length or less. Both are commonly added as solutions. Commercial formulations often contain other substances added to alter setting behaviour or for other reasons.

Most of the characteristics of conventional water reducers are shown also by superplasticizers, at least qualitatively; thus, they are more effective if added a few minutes after mixing, retard setting and increase slump loss. Retardation of set is slight with SMF but more marked with SNF. Slump

loss is considerable with both types, and is accelerated by increase in temperature. At 15°C, the enhanced fluidity typically persists for 30–60 min. Slump loss is lessened if the superplasticizer is added a few minutes after mixing, and can also be partly countered by including a retarder or, if practicable, by adding a second dose of superplasticizer before placing. Unlike conventional water reducers, superplasticizers used in normal concentrations do not cause significant air entrainment, and may even decrease the amount of entrapped air because of the greater fluidity of the mix. Air-entraining agents can be added, and must be used in higher than normal concentrations.

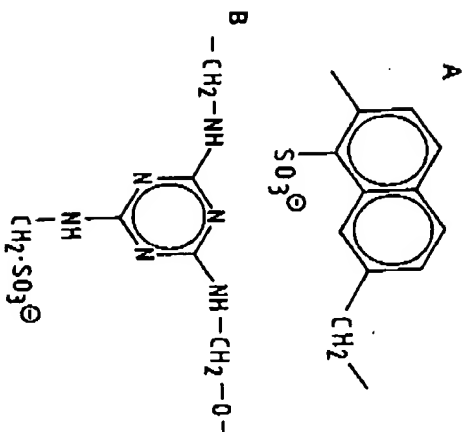


Fig. 11.3 Repeating units of the structures of superplasticizer anions: (A) naphthalene formaldehyde condensate; (B) melamine formaldehyde condensate.

11.4.3 Mode of action of water reducers and superplasticizers

The fact that the water-reducing effects of superplasticizers are similar to those of conventional water reducers used in similar concentrations suggests that the modes of action are similar, and that the essential difference is that the properties that limit the concentrations in which conventional water reducers can be used are weaker or absent in superplasticizers. These properties comprise retardation, air entrainment and in some cases flash setting.

It is widely agreed that water reduction is effected through improved dispersion of the cement grains in the mixing water; flocculation is decreased or prevented, and the water otherwise immobilized within the flocs is added

to that in which the particles can move. With superplasticizers, this can be seen with the light microscope (D44,R32), or in greater detail by SEM of rapidly frozen samples (U14) (Section 8.1.3). With some water reducers, retardation of hydration and increased air entrainment may contribute to the increase in fluidity at any given age, though with lignosulphonates, the fluidity is increased even if air entrainment is avoided through addition of tributyl phosphate (B139), and superplasticizers in normal concentrations do not entrain air.

Adsorption of the admixture on the hydrating cement grains could decrease flocculation in at least three ways (D44). The first is an increase in the magnitude of the ζ -potential; if all the particles carry a surface charge of the same sign and sufficient magnitude, they will repel each other. The second is an increase in solid-liquid affinity; if the particles are more strongly attracted to the liquid than to each other, they will tend to disperse. The third is steric hindrance; the oriented adsorption of a non-ionic polymer can weaken the attraction between solid particles.

All water reducers, including superplasticizers, appear to contain more than one polar group in the molecule, and many are polymeric. Some simple compounds that are good retarders, such as glucose, are not water reducers. Kondo *et al.* (K56) considered that polyelectrolytes were adsorbed on the solid surfaces in the ways shown in Fig. 11.4, so that some of their polar groups bind them to the solid, while others point towards the solution.

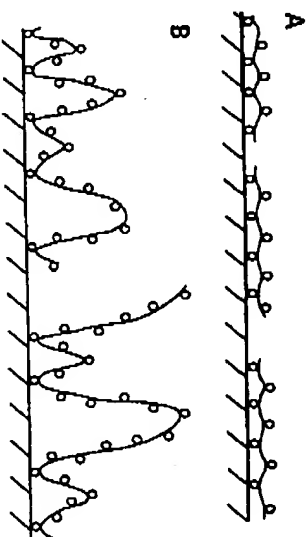


Fig. 11.4 Possible modes of attachment of polyelectrolytic anions to the surface of a particle of cement: (A) train and (B) loop modes. Circles represent negatively charged groups. After Kondo *et al.* (K56).

11.4.4 Zeta potential, rheology and nature of the sorbent phases

Ernsberger and France (E7) showed that addition of calcium lignosulphonate causes cement grains to develop a negative ζ -potential. Daimon and

Roy (D44, D45) studied the action of superplasticizers by determinations of ζ -potential and quantities adsorbed, which they related to the flow behaviour. In the absence of admixture, the charges on the grains were too small to permit reliable determinations of the ζ -potential, but with increasing contents of admixture the latter became increasingly negative, and tended towards a limit of -30 to -40 mV. Up to about 1% of SNF could be adsorbed, and the increase in ζ -potential, amount adsorbed, dispersion of the grains and increase in fluidity were all positively correlated. Daimon and Roy concluded that the increase in ζ -potential was the major cause of the improved dispersion. Further rheological studies (A25, R53) showed that superplasticizers decrease both the plastic viscosity and the yield stress. The major effect was on the yield stress, which could decrease almost to zero. Zeiler (Z11) found that, in the absence of admixtures, C_{3S} and cement developed weak negative ζ -potentials. That of C_{3A} was difficult to study due to flocculation, but appeared to be positive, becoming negative on hydration.

Kondo *et al.* (K56) considered that too high a molecular weight was undesirable, as the molecules could then form bridges between adjacent particles. In contrast, Anderson *et al.* (A26) found that for sulphonated polystyrenes, the highest ζ -potentials were obtained with material of high molecular weight, although this was not as strongly adsorbed as that of lower molecular weight. They concluded that the high molecular weight material was more likely to show loop as opposed to train adsorption (Fig. 11.4), and thus to place more of its negative charges into the diffuse double layer.

The fact that both conventional water reducers and superplasticizers are more effective if added some time after mixing provides a strong indication that adsorption probably occurs at least in part on the hydrated phases, as the anhydrous surfaces have by that time become covered with hydrating products. Chiocchio *et al.* (C57) found that the optimum time for adding was at the start of the induction period. More of the admixture seems to be taken up by the early hydration products, especially of the aluminate phase, if it is added before the early reaction has subsided.

Costa *et al.* (C58) showed that superplasticizers increase the fluidity of C_{3S} pastes much as they do that of cement pastes. Studies on individual anhydrous and hydrated compounds in aqueous and non-aqueous media indicate that calcium lignosulphonate and superplasticizers are adsorbed by C-S-H. AFm phases or CH but not by C_{3S} , C_{3A} or C_2AH_6 (R3, R35, R36, C38, M105), though they appear to be taken up by unhydrated β - C_{2S} (C59). The admixtures also enter interlayer sites of C_2AH_6 , and perhaps also of C-S-H (R55). Intercalation of organic molecules in C_2AH_6 is a well-established effect (Section 6.1.1).

Banfill (B140) noted that the amounts of superplasticizers taken up by cement were sufficient to form a layer on the anhydrous grains some 60 nm thick. He concluded that multilayer adsorption occurred and that steric hindrance was the major effect. This argument is weakened by the evidence that uptake is largely by the hydration products and that significant amounts of material are adsorbed as well as adsorbed. The bulk of the evidence indicates that increase in ζ -potential is the major effect.

11.4.5 Reasons for the enhanced dispersing power of superplasticizers

As noted earlier, the difference between superplasticizers and conventional water reducers probably lies in the weaker ability of the former to act as retarders, air-entraining agents, or causes of quick setting, which allows them to be used in higher concentrations. The low air-entraining ability can reasonably be attributed to the repeating pattern of polar groups, which provides the molecule with no suitable hydrophobic regions (K56). The reason for the weakness of the retarding power is less obvious. Weak retarding power implies that the hydration products can grow despite the presence of the sorbed material. This might happen because the latter can be assimilated into them, or because the individual bonds between sorbent and sorbate are sufficiently weak that the latter can be displaced by ions adding to the product. Equilibrium with the solution would ensure that the sorbate was readsorbed on the added material.

11.5 Inorganic accelerators and retarders

11.5.1 Accelerators of setting and hardening

Calcium chloride has long been known to accelerate both the setting and hardening of Portland cement concrete. Typically, for concrete cured at 20°C, 2% of $CaCl_2 \cdot 2H_2O$ by weight of cement might shorten the time of initial set from 3 h to 1 h and double the 1-day compressive strength. The effect on strength decreases with time, and the final strength can be reduced. Some properties related to the microstructure of the paste, such as resistance to sulphate attack, are also adversely affected. The accelerating effects are greater at low temperatures. They increase with the amount of $CaCl_2$ used, and at 4% very rapid setting may occur; 2% is probably a reasonable limit. This gives a concentration of about 0.3 mol l^{-1} in the mixing water for $w/c = 0.5$.

Calcium chloride is typically added as $CaCl_2 \cdot 2H_2O$. Chloride ion pro-